



Short communication

Effect of methanol absorption on properties of polymer composite bipolar plates for direct methanol fuel cells

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H I G H L I G H T S

- We examine the effect of the methanol absorption on properties of bipolar plates.
- The profile of the absorbed amount for PVDF increases as in Fickian diffusion.
- The thermal conductivity decreases after methanol exposure for PVDF composite.
- PPS compound exhibited a long term resistance to methanol exposure.
- Electrical conductivity is not affected by the methanol exposure for all compounds.

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The effect of the methanol absorption on thermal, mechanical and electrical properties of highly-filled graphite polymer composite plates destined for direct methanol fuel cells was investigated. Poly (vinylidene fluoride) (PVDF), Poly (phenylene sulphide) (PPS) and Poly (propylene Glycol) (PPG) compounds were considered in this study. It was shown that the absorbed amount of methanol for PVDF compound increased linearly with the square root of time as in Fickian diffusion. The methanol uptake in the saturation stage reached the value 2% after 1500 h methanol exposure. A significant change of the thermal conductivity as well as the flexural strength was reported for PVDF compound after methanol exposure, while the electrical conductivity was not altered. Additionally PPS compound exhibited a long term resistance to methanol exposure and met to a great extent the requirements defined by the US Department of Energy on the thermal and electrical conductivity. The PPS compound is a potential candidate to be used for applications as bipolar plates in direct methanol fuel cells.

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1. Introduction

The bipolar plates constitute the most important element of PEMFC (proton exchange membrane fuel cells). They are multi-functional components in a PEMFC stack, and have become recently the subject of extensive research [1–3]. Three types of material could be used for bipolar plates, metallic, pure graphite or polymer composites plates. Metallic bipolar plates of, for example, stainless steel show good mechanical stability as well as high electrical and thermal conductivity. The main disadvantage of metal plates is their susceptibility to corrosion despite an additional metallic protective coating such as niobium [1,4]. Pure graphite bipolar plates are already known for their excellent resistance to corrosion,

and their low electrical contact resistance. The disadvantages of this type of plates are their low mechanical properties, high porosity and high costs. Flexible graphite-based composite bipolar plates made from polymer/graphite mixture are considered as an attractive option for PEMFC. They offer the advantage of lower cost, rapid processing, higher flexibility and they show reduced weight in comparison to metal bipolar plates [5,6].

The polymer composite plates in PEM or direct methanol fuel cells (DMFC) can be affected by degradations due to their environment such as humidity, water, methanol or highly acidic medium after a long time of continuous operation. The humidity diffuses through the plates and deteriorates their performances. A very limited knowledge exists about the fluid absorption in bipolar plates. Jin-Chul Yun et al. [7] investigated the degradation of graphite reinforced polymer composites for PEMFC bipolar plates after hydrothermal aging caused by the water absorption. They exposed the plates to distilled water for 3000 h. The amount of

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moisture was measured by gravimetric test method. They observed a moisture absorption which occurred in composites and degraded the mechanical and electrical properties. They showed that the absorbed moisture introduces small cracks in the polymer resin. In addition they assessed that the imperfect bonding as defect or voids between polymer and graphite are likely susceptible areas for moisture absorption. Furthermore they compared the moisture absorption between polymer composites prepared with small (20 μm) and large (200 μm) graphite flakes. They found that the material prepared with large sizes of graphite flakes absorbed moisture more actively than small ones. L. Du and S.C. Jana [8] investigated the hygrothermal effect on mechanical and electrical properties of highly conductive graphite-based epoxy composite plates. They showed a small reduction of glass transition temperature (T_g) due to plasticization of epoxy network by absorbed water, while the composites maintained high electrical conductivity and good mechanical properties. Several studies were performed by various researchers to examine the effect of water absorption by using different material combinations in composites for non-fuel cell applications [9–13]. They showed that this effect changes significantly the glass transition temperature and may lead to the extraction of short chain molecules which affects the flexure modulus of the composite [13]. Furthermore M.D.H. Beg and K.L. Pickering [12] calculated the diffusion coefficient of moisture absorption of wood fibre reinforced polypropylene composites by measuring water uptake of specimens at regular time intervals and they found a value of about $\sim 2.5 \times 10^{-7} \text{ mm}^2 \text{ s}^{-1}$. In addition they observed a decrease of the thermal stability of the material after the hygrothermal aging. Zhou and Lucas [11] measured the water absorption in pure epoxy resin which reaches a saturation value of about 7% after 1000 h storage in water. They observed Fickian diffusion behavior and related it to physical binding of water molecules with epoxy resins composites through hydrogen bonding.

During DMFC operation, the polymer composites bipolar plates are exposed to methanol liquid. After several thousand hours of continuous operation, the methanol can penetrate through the plate and then decrease the thermal, electrical and mechanical properties of the material. Bipolar plates devoted to be used in DMFC should show long term resistance to methanol absorption and thermal degradation.

The objective of the present work is to develop and characterize conducting polymer composite plates for direct methanol fuel cell applications. The effect of the exposure of bipolar plate composites to methanol on the thermal stability, thermal conductivity, electrical conductivity and mechanical properties (flexural strength) was investigated. For these purposes three kinds of graphite polymer composites were developed and characterized before and after the methanol exposure. In-plane electrical conductivity, mechanical properties, thermal stability and through thermal conductivity using Laser Flash technique were determined.

2. Experiment

2.1. Material

In this work three kinds of graphite polymer composite bipolar plates were developed. Three polymer matrixes were used for the preparation of the plates: Poly (phenylene sulphide) (PPS), Poly (vinylidene fluoride) (PVDF) and Poly (propylene Glycol) (PPG). A high content of graphite (Gr) ($\sim 85 \text{ wt } \%$) was mixed intensively with the polymer. The density of Gr is 2.2 g cm^{-3} and its average particle size is $76 \mu\text{m}$. The polymer and the fillers were first dried and mixed in a kneader and then placed in hydraulic compression press and heated to the melting temperature and cooled carefully.

2.2. Thermal properties

The thermogravimetric analyser (TGA Q5000, TA Instrument) was used to determine the thermal degradation temperatures T_1 and T_2 . The temperature T_1 represented at 5% weight loss and T_2 corresponded to the maximum rate of weight loss [14,15]. The measurements were carried out under nitrogen atmosphere to avoid additional oxidation. A constant heating rate (10 K min^{-1}) was maintained between 20°C and 1000°C . In addition the modulated differential scanning calorimetry (MDSC Q2000, TA Instrument) technique was employed in order to obtain the glass transition temperature T_g and the specific heat capacity c_p . The MDSC-measurements were carried out under nitrogen atmosphere with a heating rate of 3 K min^{-1} .

2.3. Measurement of in-plane electrical conductivity

The in-plane (bulk) electrical conductivity was measured by the conventional four probe method. The measurements were performed at room temperature using a cylindrical four point probe head and RM3000 Test Unit from Jandel Engineering Limited. The RM3000 can supply constant currents between 10 nA and 99.99 mA, and measure voltages from 0.01 mV to 1250 mV. The electrical conductivity σ of the sample was calculated according to [16]:

$$\sigma = \left[2\pi \times \frac{U(V)}{I(A)} \times G\left(\frac{w}{s}\right) \right]^{-1} \quad (1)$$

where s is the probe spacing ($s = 1 \text{ mm}$), w is the thickness of the sample, U is the voltage, I is the current and G is the correction geometric factor. The thickness of the sample is about 3 mm.

2.4. Measurement of thermal conductivity

In this work the thermal conductivity of the materials was determined by combining the Laser Flash technique from Netzsch (427) and the modulated differential scanning calorimetry DSC technique mentioned in Section 2.2. The thermal conductivity λ is related to the thermal diffusivity D according to:

$$\lambda = DT \times c_p \times \rho \quad (2)$$

where c_p is the specific heat capacity and ρ is the volume density. The density ρ is in this work assumed to be independent of the temperature. The thermal diffusivity D was determined by Laser Flash technique and c_p by modulated DSC technique. Both measurements were performed within the temperature range 20°C – 150°C by using a heating rate of 3 K min^{-1} . The measurements of the thermal diffusivity were carried out on samples having cylindrical shape with a diameter of 12.7 mm and thickness of 1.5 mm. The sizes of the sample used for MDSC technique are 5 mm in diameter and 1 mm in thickness. Fig. 1 showed an example of the evaluation of the thermal conductivity of PPS composite. Fig. 1(a) displayed both curves of thermal diffusivity D and specific heat c_p against the temperature. Both c_p - and D -curve showed distinctive trends. The D values decrease with increasing temperature, while c_p values increased. By applying Eq. (2), the thermal conductivity λ was calculated and plotted in Fig. 1(b). The value of λ at room temperature for PPS composite is $21.2 \text{ W m}^{-1} \text{ K}^{-1}$. A very slight drop of λ is observed at high temperatures.

2.5. Mechanical properties

The three-point bending flexural technique according to DIN EN ISO 178 was performed at room temperature in order to obtain the

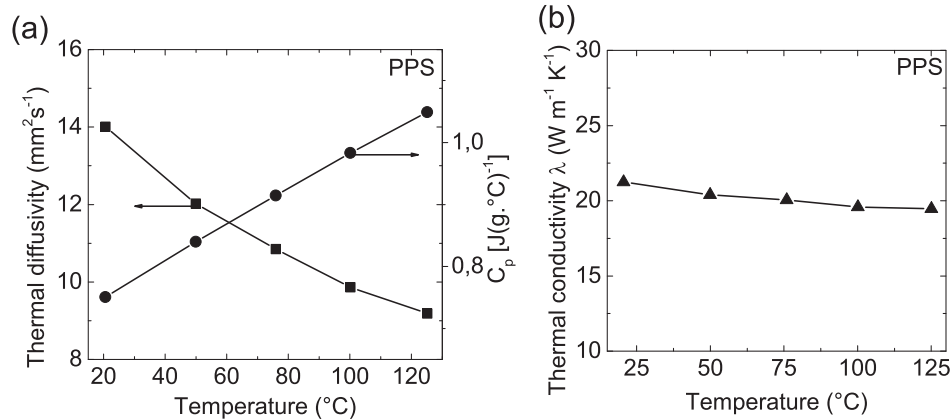


Fig. 1. Both T -dependent thermal diffusivity (square symbol) and specific heat (circle symbol) (a) and thermal conductivity against the temperature (triangle symbol) (b).

flexural strength of the materials. Rectangular specimens were cut out for flexural testing. For these tests, the support span L was calculated using a ratio L/d of 16:1 where d is the depth of the specimen.

2.6. Methanol absorption test

Methanol absorption tests were performed at room temperature for all samples. The specimens with 3 cm wide and 10 cm length were individually immersed in methanol with high purity degree from fuel cartridges. The absorption of the methanol was measured gravimetrically as a function of time. Indeed the samples were removed after 4, 16, 49, 85 up to 5000 h of exposure, dried and weighed using a Sartorius balance (0.1 mg accuracy), and finally compared with the initial weight in order to describe the characteristics of the methanol uptake in the material.

3. Results and discussion

3.1. Methanol absorption behavior

The study of the methanol's absorption was carried out by the absorption tests, in which the methanol uptake is measured gravimetrically. A continuous exposure on methanol could cause a fast aging of the plates leading to the degradation of their performance. The absorption tests were carried out on PVDF, PPG and PPS composite plates in order to determine their response after about 5000 h of methanol exposure. The degree of absorption of

methanol was measured several times during the test until reaching the equilibrium in order to study the mechanisms of the diffusion in the composite. The methanol uptake content during the immersion was calculated from the following equation

$$Wt(\%)(t) = \frac{Wt(t) - Wt(t = 0)}{Wt(t = 0)} \times 100 \quad (3)$$

where $Wt(\%)$ is the percent weight change at the time t , $Wt(t)$ is the weight of the specimen at time t , and $Wt(t = 0)$ is the initial weight of the specimen before immersion.

For the case of non-steady state diffusion, the solution from Fick's second law can be expressed by Dhakal et al. [9]:

$$D = \frac{\pi}{16} \left(\frac{h}{Wt_{\max}} \right)^2 \left(\frac{Wt(t_1) - Wt(t_2)}{\sqrt{t_1} - \sqrt{t_2}} \right)^2 \quad (4)$$

where D is the diffusion coefficient, $Wt(t_1)$ is the weight change at the exposure time t_1 , $Wt(t_2)$ is the weight change at the exposure time t_2 , h is the thickness of the specimen and Wt_{\max} is the maximum methanol absorption.

Fig. 2(a) displays the time-depending percent weight change $Wt(\%)$ between 0 and 5000 h. The values of $Wt(\%)$ for the PVDF composite abruptly increased between 0 and 260 h and then reached a plateau by showing an apparent saturation value of about 2%. A slight rise of the mass uptake was observed for PPG composite, while the mass uptake for PPS composite was almost zero within the time range from 0 to 5000 h. The reason of the large

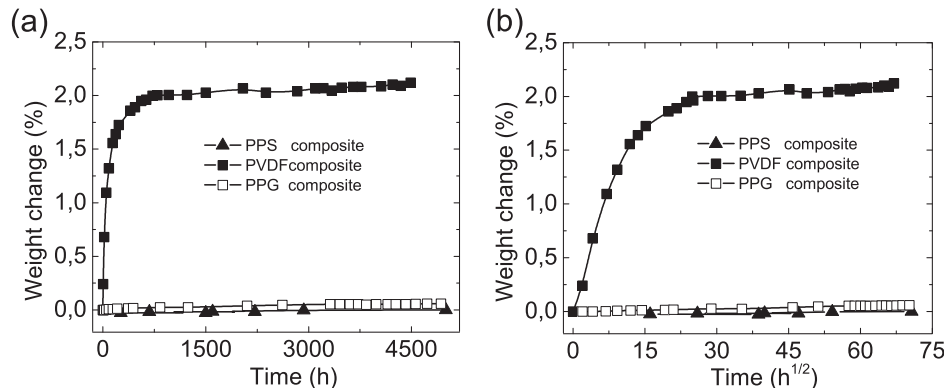


Fig. 2. Time-dependent percent weight change for PPS (triangle), PPG (open square) and PVDF (full square) (a) and square root time-dependent percent weight change for the three samples.

change in methanol absorption for PVDF composite could be caused by the lack of adhesion and compatibility between filler and polymer network. In addition the creation of imperfections like voids, which can originate during the processing of the material, allowed the permeation of methanol through the specimen. Ling Du and S.C. Jana [8] investigated the effect of water absorption (hygrothermal aging) on properties of conductive epoxy composites for application as bipolar plates. They showed a maximum water uptake of about 1.8% for epoxy composite, while they found a value of 4.3% of the water uptake for the unfilled epoxy. They attributed this difference to the presence of graphite and carbon black which make the composite more hydrophobic in nature [8]. The values of W_t (%) against the square root of time are plotted in Fig. 2(b). It can be observed that the methanol uptake for the PVDF composite followed the Fickian diffusion model, where the absorbed amount of methanol increased linearly with the square root of time in the early periods and gradually reached the equilibrium at the value of about 2%. The diffusion parameter D was determined from the initial slope in Fig. 2(b) by applying Eq. (4). A value of D equals $7.6 \times 10^{-6} \text{ mm}^2 \text{ s}^{-1}$ was found for PVDF composite. This value was one order of magnitude higher than the diffusion parameter ($0.46 \times 10^{-6} \text{ mm}^2 \text{ s}^{-1}$) obtained for epoxy composite plates immersed in water [8]. Usually the high diffusion parameter is related to a high amount of the pure polymer in the composite. In this case the higher diffusion parameter D due to the methanol uptake was obtained for PVDF composite although the amount of the polymer (20 wt%) was lower compared to that (50 wt%) in epoxy composite [8]. The high value of D for PVDF composite is probably due to the type of the polymer matrix used during the processing of the composite as well as to the nature of the liquid in which the sample was stored.

3.2. Thermal stability

The thermal stability of the composites was investigated after methanol exposure of 1500 h. The values representing the thermal degradation T_1 and T_2 obtained from TGA as well as the values of glass transition T_g measured by DSC are summarized in Table 1. The results before and after methanol exposure were considered. The thermal degradation T_1 and T_2 decreased after methanol exposure for all compounds (Figs. 3 and 4). A pronounced decrease is observed for PVDF compound showing a shift of about 35 °C to lower temperature values (Fig. 3) which mean a significant drop of the thermal stability for PVDF compound. A similar tendency is reported for polymer composite plates after hygrothermal aging [17]. In addition insignificant change was observed for the T_g values after methanol exposure for PVDF, PPG and PPS compounds (Table 1).

3.3. Thermal conductivity

One of the main functions of the bipolar plate is the transfer of the waste heat to a cooling channel in order to maintain constant operating temperature in the fuel cell systems and to prevent an eventual degradation of the proton exchange membrane. Therefore

Table 1
List of the values of T_1 , T_2 and T_g before and after methanol exposure.

Compound	Before methanol exposure			After methanol exposure		
	T_1 (°C)	T_2 (°C)	T_g (°C)	T_1 (°C)	T_2 (°C)	T_g (°C)
PVDF	470	481	45.7	436	449	45.5
PPS	551	554	96	545	541	95
PPG	454	472	45	434	464	44

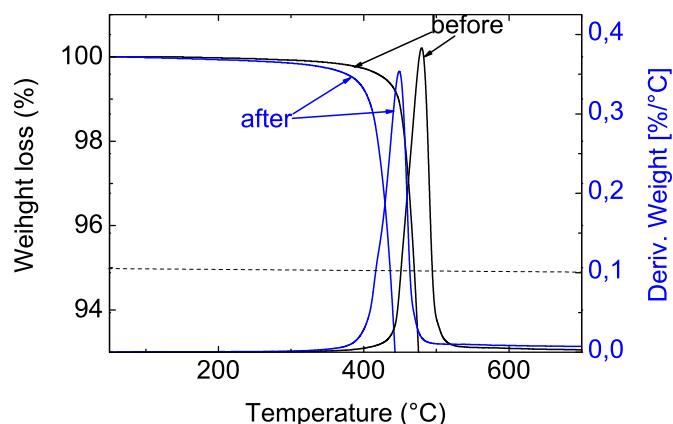


Fig. 3. Both T -dependent weight loss (black) and differential weight loss (blue) before and after methanol exposure for PVDF compound. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a high thermal diffusivity is necessary to move the heat through the plates rapidly. As mentioned previously the through-plane thermal conductivity is calculated from the thermal diffusivity via Eq. (2). For suitable bipolar plates the limit value of the thermal conductivity defined by the US Department of Energy (DOE) was fixed as $10 \text{ W m}^{-1} \text{ K}^{-1}$ [18]. The compounds PPS, PPG and PVDF were immersed in methanol for 1500 h. After drying, the thermal conductivity λ was evaluated. The results plotted in Fig. 5 showed that the value of the thermal conductivity for all compounds exceeded $10 \text{ W m}^{-1} \text{ K}^{-1}$. Fig. 5(a) showed the thermal conductivity for both stages before and after methanol exposure for both PPS and PPG compounds. A slight drop of λ against the temperature is observed for PPS in both stages. The effect of methanol exposure showed a decrease of 5% of the thermal conductivity λ at 75 °C. For the PPG compound the decrease against the temperature is more significant. At a temperature of 75 °C the reduction reached 11% after methanol exposure for PPG compound. Fig. 5(b) displayed the thermal conductivity of PVDF compound before and after methanol exposure as function of the temperature. It can be observed that λ values drastically decreased at high temperature, especially after 100 °C before methanol exposure, while λ values showed almost a flat profile between 20 °C and 120 °C after methanol exposure. In comparison with PPS and PPG compounds, PVDF compound revealed a decrease of λ value of about 30% at the temperature 75 °C after methanol exposure. This may be due to the high methanol uptake which located in voids in the material leading to a resistance against the heat transfer.

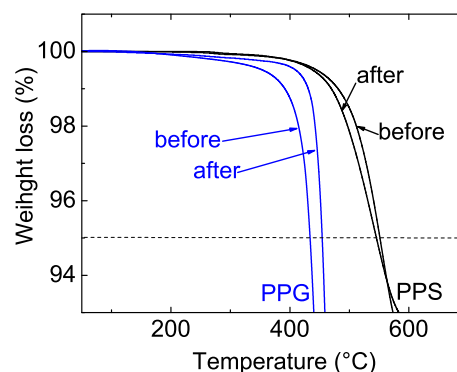


Fig. 4. T -dependent weight loss before and after methanol exposure for PPG and PPS compound.

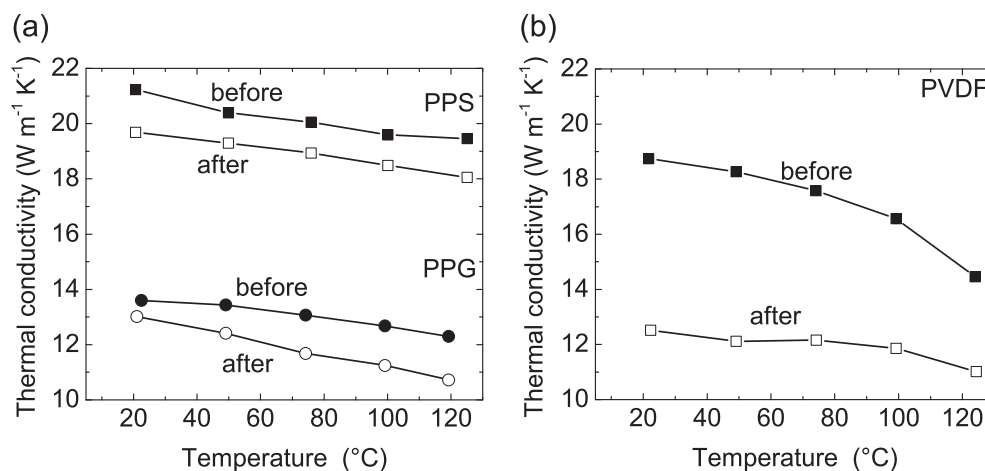


Fig. 5. T-dependent thermal conductivity before and after methanol exposure for PPG (open and full circle symbol) and PPS (open and full square symbol) (a) and for PVDF (b).

3.4. In-plane electrical conductivity

In-plane electrical conductivity σ was performed on three samples. This property is of crucial importance since a good transport of electrons through the bipolar plates is ensured in the circuit of the fuel cells by high values of electrical conductivity. For suitable plates the limit value of the electrical conductivity, defined by DOE [18] has to be 100 $S cm^{-1}$ at least. The values of σ are plotted in Fig. 6 against the square root of time for all samples. The electrical conductivity was measured during the methanol exposure at different interval time until 1500 h. The electrical conductivity was not altered by the methanol exposure although a high methanol uptake was measured for PVDF compound. The compounds PPS and PPG showed small variations of σ values during the aging. Similar result was found by Du et al. after water exposure for 3600 h for epoxy composite plates [8]. In addition, it can be seen that PVDF had the highest value of the electrical conductivity ($\sim 180 S cm^{-1}$), which exceeds the limit value defined by DOE. However the electrical conductivity of PPG compound is lower than 50 $S cm^{-1}$. The requirements of US DOE in this case were not achieved. PPS compound exhibited a high electrical conductivity which varies between 120 $S cm^{-1}$ and 124 $S cm^{-1}$ during methanol exposure.

3.5. Mechanical properties

Bipolar plates support the membrane electrode assembly and are exposed to the constant effect of the compressive load of the

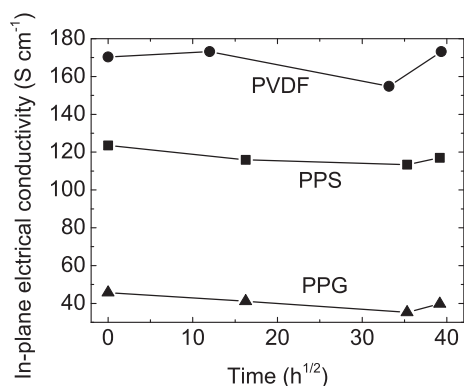


Fig. 6. Square root time-dependent in-plane electrical conductivity for the three samples during methanol exposure.

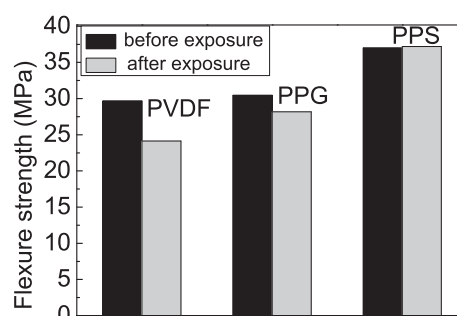


Fig. 7. Flexural strength for all samples before (black) and after (gray) methanol exposure.

PEMFC. For this reason the determination of good or adequate mechanical properties is important. The three-point bending technique was performed at room temperature on all samples in order to obtain the flexural strength parameter R . The values of the parameter R before and after exposure were illustrated in Fig. 7 after 1500 h methanol exposure. Fig. 7 showed a significant decrease of the parameter R for PVDF compound, while the value of R for PPS compound remained the same. The flexural strength was not reduced significantly for PPG compound. The high content of methanol uptake through the PVDF compound probably affected the mechanical properties of the material.

4. Conclusion

The effect of the methanol absorption on thermal, mechanical and electrical properties of highly-filled graphite polymer composite plates destined for direct methanol fuel cell was investigated. It was demonstrated that the PVDF compound followed linear Fickian diffusion profile. A high amount of 2% of the methanol uptake was obtained for PVDF compound. A very slight methanol uptake was shown for PPG compound, while no diffusion of methanol was observed for PPS compound. A high drop of the thermal conductivity was observed for PVDF compound after methanol exposure. This was attributed to the high methanol uptake measured in the material causing a reduction of the thermal conductivity. The electrical conductivity was maintained during the methanol exposure for all samples. The electrical conductivity was not affected during the aging of PVDF compound although a high methanol uptake was found. However a significant decrease of the flexural strength was

measured after exposure for PVDF compound. Finally it was concluded that PPS compound exhibited a long term resistance to methanol exposure and met to a great extent the requirements defined by the US Department of Energy on thermal and electrical conductivity. The PPS compound seems to be suitable to be used for applications as bipolar plates in direct methanol fuel cells.

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